LA-UR-01-6526

Approved for public release; distribution is unlimited.

Title: **Thermal Stability of Self-Supported Metallic Multilayered Thin Films**

Author(s): A. Misra, H. Kung and R.G. Hoagland

Submitted to:

http://lib-www.lanl.gov/la-pubs/00796506.pdf

Thermal Stability of Self-Supported Metallic Multilayered Thin Films

A. Misra, H. Kung and R.G. Hoagland,
Materials Science and Technology Division, MS G755,
Los Alamos National Laboratory, Los Alamos, NM 87545

ABSTRACT

The morphological stability and strength retention following elevated temperature exposure or thermal cycling will be crucial in exploiting the extremely high strengths of nanolayered materials in advanced engineering applications. The effects of elevated temperature (≤ 800 °C) vacuum annealing on the morphological stability and mechanical properties of sputter deposited Cu-Nb multilayers with 75 nm bilayer period are reported here. Even after 800 °C/ 1 hour anneal, the continuity of the layered structure is maintained and the bilayer periods are unchanged. The in-plane grain sizes in both Cu and Nb coarsened but were anchored at grooved boundaries preventing further growth. For a constant bilayer period, the effect of increasing the in-plane grain size on the multilayer hardness is found to be insignificant. After annealing, the layers are observed to be offset by shear along a vertical plane at the triple point junctions that have equilibrium groove angles aligned in a zig-zag pattern. A new mechanism is proposed for the evolution of this "anchored" structure that is resistant to further morphological instability.

INTRODUCTION

Multilayered thin films on substrates are used in a variety of applications such as x-ray mirrors, magnetic recording media and heads, diffusion barrier coatings, wear resistant coatings, etc. Thermal stability of these films has been studied mostly for the instability mechanisms involving interdiffusion in miscible layers, chemical reaction to form a new phase/compound or phase transformation (e.g., amorphous to crystalline), etc. Recent studies have shown that metallic multilayers, composed of alternating layers of soft metals, typically possess unusually high strengths when the bilayer periods are on the order of a few to a few tens of nanometers [1,2]. In addition to coatings on substrates, these high-strength metallic multilayers may also have applications as self-supporting components.

Most studies of the morphological stability of fiber or lamellar composites have been conducted for materials where the microstructural features are on the micron-scale. These studies show that although lamellar composites are relatively more stable than fiber composites, significant morphological instabilities may still occur in layered materials such as pearlitic steels, γ/α_2 titanium aluminides, rolled Ni-W, etc [3,4]. Recently, Josell and Spaepen [5] have studied the stability of near-micron scale multilayered films, primarily through creep testing, and observed layer pinch-off due to grain boundary grooving as a major instability mechanism. These studies indicate that complete degradation of the multilayer structure is often possible during short anneals at elevated temperatures. Clearly, more detailed studies of the thermal stability of nano-scale multilayers are needed to elucidate the mechanisms of morphological instability and identify microstructure design schemes towards stable structures.

In this investigation, we have studied the morphological stability of self-supported, room temperature sputtered nano-scale Cu-Nb multilayered films in the temperature range of 500 – 800 °C. Cu and Nb do not form any intermetallic compounds, there is insignificant mutual solubility and no phase transformations at the annealing temperatures chosen. The microstructural evolution and hardness changes following annealing are reported here.

EXPERIMENTAL PROCEDURES

Cu-Nb multilayers with equal Cu and Nb layer thicknesses (throughout this article, the samples are identified with their layer thickness which is one-half of the bilayer period) of 75 nm were sputter deposited on glass or Si substrates at room temperature. Sputtering was dc magnetron with 4 mTorr Ar pressure, 10 cm substrate-to-target distance and 100 W and 200 W power applied to 10 cm diameter Cu and Nb sputtering targets respectively. The chamber was evacuated to a base pressure of ~2 x 10^{-8} torr prior to deposition. The total number of bilayers deposited was 50, resulting in a total sample thickness of 7.5 μm. After deposition, the multilayered films were peeled from the substrates and the self-supported samples subjected to 1 hour annealing at temperatures of 500, 600, 700 and 800 °C under vacuum of ≤ 1 x 10^{-7} torr. Microstructures were studied by cross-section transmission electron microscopy (TEM) using a Philips CM30 microscope at 300 kV. Hardness and modulus of the films, epoxy-bonded to Si substrates after annealing, were measured with a NanoIndenter II using the continuous stiffness method. The indentation depths were in the range of 0.25 to 0.5 μm.

RESULTS

As-synthesized Microstructures

The microstructure of the as-deposited Cu-Nb 75 nm multilayer is shown in Fig. 1(a) as a cross-section bright field (BF) TEM micrograph, along with the selected area diffraction pattern (SADP) in Fig. 1(b). Note the nanocrystalline structure of the layers with columnar grains, i.e., most grain boundaries are normal to the interface. The in-plane grain size is on the order of the layer thickness (75 nm) for Cu and slightly lower for Nb. The SADP indicates a {110}bcc // {111}fcc // interface plane texture in these multilayered films.

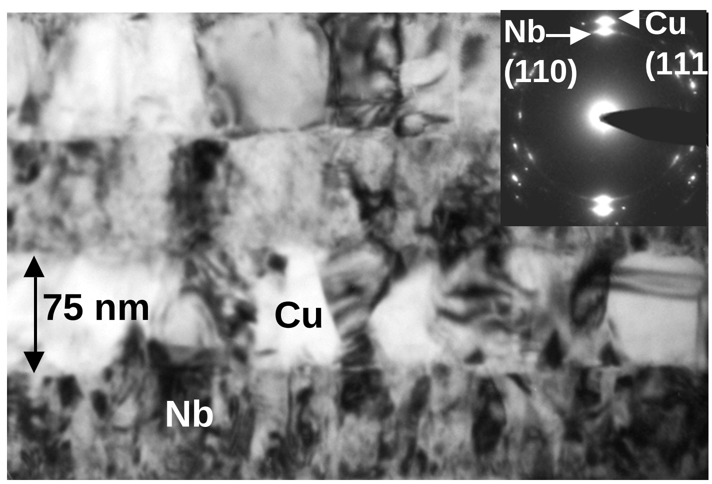

Fig. 1 BF TEM micrograph and the corresponding SADP showing the textured polycrystalline microstructure, in cross-section, of the as-deposited Cu/Nb multilayer.

Annealed Microstructures

Keeping the initial layer thickness fixed at 75 nm, the microstructural evolution following 1 hour anneals at 600, 700 and 800 °C is shown in Fig. 2(a)-(c) respectively. Some significant features after 600 °C anneal are (Fig. 2(a)): (i) layer structure is not disintegrated (i.e., no significant geometric rearrangement of the layered structure), (ii) no measurable change in the 75 nm layer thickness, and (iii) in-plane grain size has increased. Perhaps the most significant feature is that at some regions, (e.g., the region marked by arrows in Fig. 2(a)), the grain boundaries in Cu and Nb are aligned along a vertical line. The significance of this observation is discussed later in the paper. From other images not shown here, most grains in the Nb layer were observed to be ~75-100 nm while most grains in the Cu layer were ~150-200 nm after 600 °C anneal. The {110}Nb // {111}Cu texture was retained after annealing.

Fig. 2(b) shows the microstructure of the Cu-Nb multilayered film after 700 °C/ 1 h anneal. Even at 700 °C, no disintegration of the layered structure or any coarsening of the bilayer period is detected. The most significant microstructural change is the facetted appearance of grain boundaries and offsets between layers along an approximate vertical plane with an attending shear effect of the layers along this plane. These planes where shear offsets are observed presumably coincide with the regions shown in Fig. 2(a) where grain boundaries in Cu and Nb appeared to have aligned. The grains in both layers are approximately equal in size and typically, ~375-400 nm wide.

Fig. 2(c) shows the microstructure of the Cu-Nb multilayered film after 800 °C/ 1 h anneal. Even at a temperature of ~80% of the melting point of Cu, the layer structure is maintained. Also, no significant coarsening of the layers is observed. Thermal stresses, upon cooling, have led to significant dislocation activity in both layers. The in-plane grain sizes are similar to 700 °C indicating that increasing the anneal temperature from 700 to 800 °C did not significantly accelerate grain growth. In fact, places where layers are offset along a vertical plane serve as "anchor" points thereby limiting further grain growth. Once again, faceted grains at triple or quadruple points are observed. However, the layer offsets are about the same as after 700 °C, indicating that near-equilibrium groove angles are formed at triple points and continued grooving to split the layers does not occur.

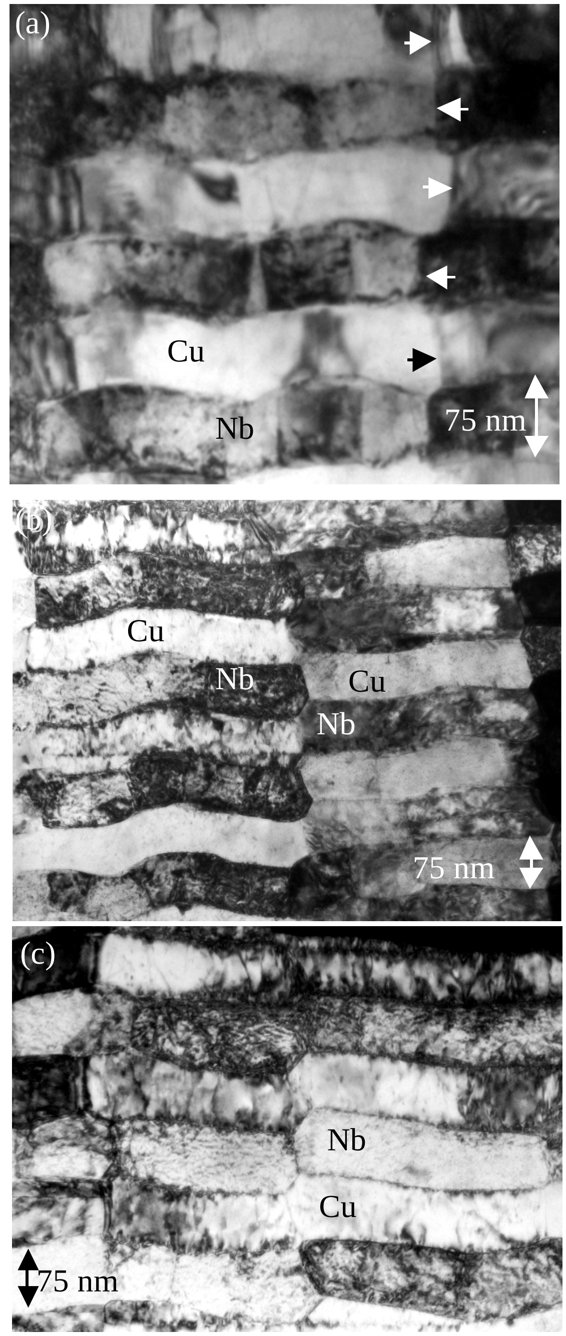

Fig. 2 BF TEM micrographs showing the cross-sectional views of the microstructures of 75 nm Cu-Nb multilayers after (a) 600 ¡C, (b) 700 ¡C, and (c) 800 ¡C anneals. Note the alignment of grain boundaries along a vertical line (marked with arrows in (a)), and grooving and shear of layers at triple points in (b).

The equilibrium groove angle is related to the grain boundary ($\gamma_{\square\square}$) and interface energies (γ_{int}) as follows (Fig. 3):

$$\gamma_{\square\square} = 2\gamma_{int} \cos \theta \qquad (1)$$

where θ is one-half the groove angle. The Nb-Nb grain boundary makes an angle of 120° with the two adjoining Cu-Nb interfaces. Hence, $\gamma_{Nb\text{-}Nb} \approx \gamma_{Cu\text{-}Nb}$. Similarly, Cu-Cu grain boundaries made angles of 126-130° with the Cu-Nb interfaces, indicating that $\gamma_{Cu\text{-}Cu} \approx \gamma_{Cu\text{-}Nb}$.

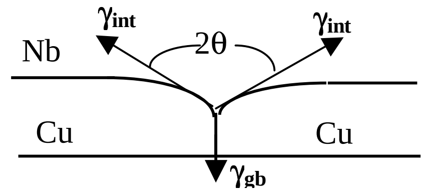

Fig. 3 Schematic showing the force balance at a triple point that determines the equilibrium groove angle.
Cos θ = $\gamma_{gb}/2\gamma_{int}$.

<u>Multilayer Hardness</u>

The hardnesses of the Cu-Nb 75 nm multilayer before and after annealing are compared in Fig. 4. In the as-deposited state the hardness was 3.4 ± 0.3 GPa. After annealing at different temperatures in the range of 500-800 °C, no significant change in either the hardness or the modulus was observed. These results indicate that the increase in the in-plane grain size does not affect the hardness of these multilayers. Thus, the hardness enhancement generally observed with decreasing layer thickness in the Cu-Nb multilayers [1,2] is primarily due to the resistance to slip transmission from the Cu-Nb interfaces, with a relatively smaller contribution from the in-plane grain boundaries. This observation is consistent with atomistic modeling of nanolayered metals that indicates that these materials derive their strength from the transmission of single dislocations across the interphase interfaces [6].

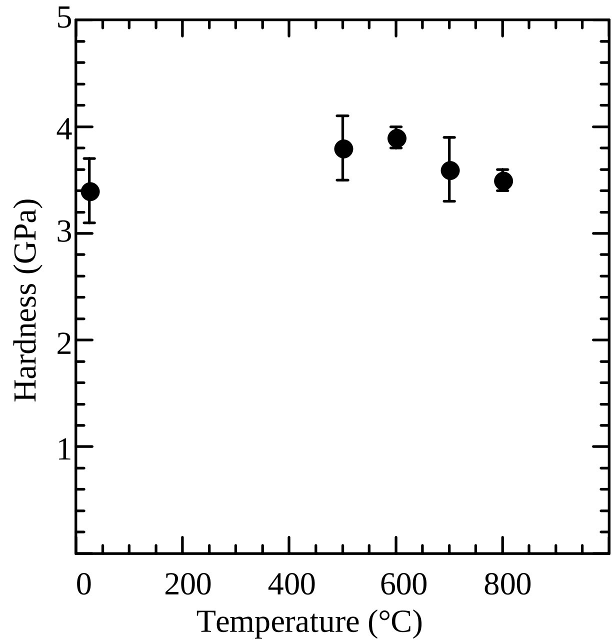

Fig. 4 Hardness of 75 nm Cu/Nb multilayers as a function of annealing temperature. Note the insignificant change in hardness with annealing.

DISCUSSION

Thickness perturbations (Rayleigh instability [7]) that lead to spheroidization of rods embedded in a matrix are common in fiber composites. Spheroidization of lamellar composites is a two-step process (plates to rods, and then rods to spheres) and hence, the plate morphology is likely to resist spheroidization better than rods [8]. Typically, morphological instability in a lamellar structure starts at the edge of a finite plate (i.e., lamellae termination points) embedded in a matrix. Since there are no lamellae termination points in the thin film multilayers investigated here, any morphological change during annealing is expected to initiate with thermal grooving at triple points (intersection of in-plane Cu-Cu or Nb-Nb grain boundaries with the Cu-Nb interface) as shown schematically in Fig. 3 [5,9]. The equilibrium at these triple points is determined as shown in Fig. 3 by a simple force balance that defines the groove angle following eq. (1). Note from the microstructure shown in Fig. 1 that in the as-deposited films, the in-plane grain boundaries are almost orthogonal to the interphase interface (i.e., θ=90°), resulting in an energetically unfavorable configuration. Thus, it is expected that elevated temperature annealing will result in diffusive mass transport along boundaries so as to establish an equilibrium groove angle at the triple points. If the depth of the groove is greater than the layer thickness, then the grooving will split the layers creating lamellae termination points which can then begin to spheroidize. Hence, the critical event for the multilayered film stability is the grooving kinetics and how quickly the layers are split and this is discussed next.

For multilayered thin films, the grooving kinetics may be described by the following equation derived by Josell and Spaepen [5]:

$$x^3 = (D_L h + D_B \delta)\frac{\gamma \Omega t}{hkT} \qquad (2)$$

where x is the groove depth, D_L is the lattice diffusion, D_B is the grain boundary diffusivity, δ is the boundary thickness, γ is the interface free energy, Ω is the atomic volume, k is the Boltzman constant, T is the annealing temperature and t is annealing time. Using $D_B\delta$ for Nb = 6 x 10^{-16} mm^3/s and D_L = 3 x 10^{-21} mm^2/s at 973 K, $\gamma_{Cu/Nb} \approx 1$ J/m^2, h = 75 nm, t = 3600 s and Ω = 1.8 x 10^{-20} mm^3, x is obtained as ≈ 30 nm. This compares quite well with the experimentally observed groove depths of ≈ 35-40 nm shown in Fig. 2(b). Since grooving requires mass transport of both Cu and Nb, the kinetics is controlled by the slower of the two (Nb). Note that at the anneal temperatures, $D_B >> D_L$ for Nb. Thus, lattice diffusion of Nb can be ignored.

The above model explains only part of the microstructural evolution shown in Fig. 2, i.e., the grooving, and not the offset or shear of layers along a vertical plane at triple points. We propose a mechanism (Fig. 5) to interpret the observed morphological stability of the Cu-Nb multilayers. Consider the case shown in Fig. 5(a) where the corresponding grains I and II in Cu and Nb have the low energy {110}Nb // {111}Cu interface but not the interface segment 'ab' where grain I in Cu and grain II in Nb form the interface. Such an initial structure is consistent with Fig. 1 since Cu and Nb do not have the same in-plane grain size. At elevated temperatures, in-plane grain boundary migration occurs in the direction of arrows to remove the high-energy segment 'ab'. Note that the grain boundary migration of Cu will be significantly faster than that of Nb. The in-plane grain boundary migration leads to the situation shown in Fig. 5(b) where an

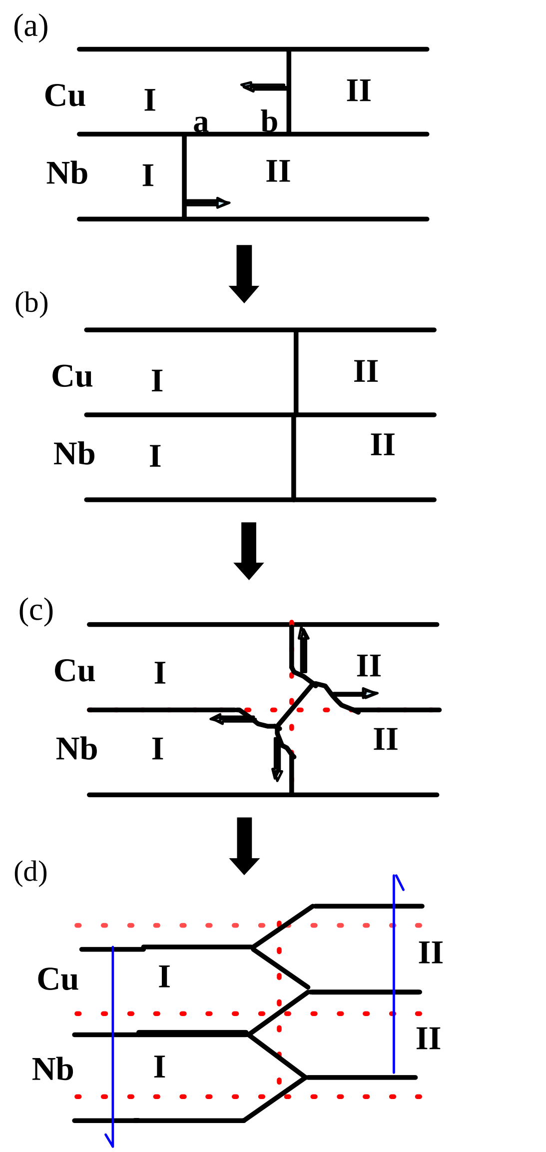

Fig.5 Schematic of the morphological evolution observed in nano-scale Cu-Nb multilayers upon elevated temperature annealing.

energetically unfavorable quadruple point has been created as the sideways migration leads to an overlap of grain boundaries (compare Fig. 2(a) with Fig. 5(b)). As a result, the unstable quadruple point breaks into two triple points (Fig. 5(c)). Diffusive mass transport at both of these triple points along the directions marked by arrows in Fig.5(c) will occur to establish equilibrium groove angles, resulting in a final configuration shown in Fig. 5(d) where the layers are sheared across a vertical plane formed by the overlap of sideways migrating grain boundaries. The final structure (compare Fig. 2(b) with Fig. 5(d)) is found to be extremely stable due to the sheared layers with equilibrium groove angles at triple points acting as "anchor" points and preventing further grain growth or layer splitting. This "anchored" structure resulted after 700 °C/ 1 hour annealing (Fig. 2(b)). Annealing at temperatures higher than 700 °C (Fig. 2(c)) or for longer times at 700 °C to 60 hours (results to be presented in a future article) did not result in any further morphological instability. Thermal stability of these multilayers as a function of the bilayer period is being studied and will be presented in a future article.

SUMMARY

Sputter-deposited nanoscale Cu-Nb multilayers exhibit excellent microstructural stability and hardness retention following vacuum annealing at temperatures up to 800 °C. Thermal grooving at grain boundaries was observed after 700 and 800 °C annealing. The Josell-Spaepen [5] diffusion model, using Nb grain boundary diffusion as rate controlling, describes the grooving kinetics. However, thermal grooving did not result in layer pinch-off. Rather, the shear of layers across the grooving triple points resulted in an "anchored" structure resistant to further morphological instability. A mechanism for the evolution of this stable microstructure is proposed. The hardness retention, in spite of coarsened in-plane grains, suggests that the hardness is primarily determined by the spacing of the Cu/Nb interfaces that remained unchanged after annealing.

ACKNOWLEDGEMENTS

This work is supported by the Office of Basic Energy Sciences, Department of Energy. Authors acknowledge discussions with F. Spaepen, J.D. Embury, J.P. Hirth, T.E. Mitchell, P. Anderson and M. Nastasi.

REFERENCES

1. B.M. Clemens, H. Kung and S.A. Barnett, MRS Bulletin, **24**, 20, February (1999).
2. A. Misra and H. Kung, Advanced Engineering Materials, 217, April (2001).
3. J.C. Malzahn Kampe, T.H. Courtney and Y. Leng, Acta Metall., **37**, 1735 (1989).
4. G. Sharma, R.V. Ramanujan and G.P. Tiwari, Acta Mater., **48**, 875 (2000).
5. D. Josell and F. Spaepen, MRS Bulletin, **24**, 39, February (1999).
6. R.G. Hoagland, T.E. Mitchell, J.P. Hirth and H. Kung, Phil Mag A, 2002, in press.
7. Lord Rayleigh, Proc. London Math. Soc., **10**, 4 (1878).
8. N. Sridhar, J.M. Rickman and D.J. Srolovitz, Acta Mater., **45**, 2715 (1997).
9. A.C. Lewis, A.B. Mann, D. van Heerden, D. Josell and T.P. Weihs, Mat. Res. Soc. Symp. Proc., **652** (2001), in press.